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ORIGINAL ARTICLE

Pre-concentration and determination of zinc in water samples by ligand assisted pseudo stirbar hollow fiber solid/liquid phase microextraction

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KEYWORDS

Anodic stripping voltammetry;
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Abstract Pre-concentration and determination of Zn (II) across a ligand assisted pseudo stirbar hollow fiber solid/liquid phase microextraction method in water samples has been investigated. All detections were carried out by differential pulse anodic stripping voltammetry (DPASV). The method involves microextraction and pre-concentration of Zn (II) on the pseudo stir bar hollow fiber. Then desorption has been done using suitable solvent containing suitable ligand as complexing agent. The optimized conditions were obtained. The relationship between the peak current and concentration was linear over the range of 0.05–500 ng mL^{-1}. The limit of detection was 0.015 ng mL^{-1}. Under the optimized conditions, the pre-concentration factor is 5140. The applicability of the developed technique was evaluated by application to spiked, environmental water samples.

1. Introduction

Monitoring trace metals like zinc in water samples is important for human health and the environment. Zinc is a metal with a brilliant shine bluish-gray color (Nriagu, 1980). It is chemically active and is an essential trace element involved in antioxidant reactions. It can enhance the human immune system. Vegetarians should be conscious of ensuring an adequate intake of zinc. Zinc occurs in small amounts in almost all igneous rocks. The principal zinc ores are sulfides (Elinder, 1986). The natural zinc content of soils is estimated to be 1–300 mg/kg (Nriagu, 1980). One of the primary goals of health protection communities is that all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water.

In natural surface waters, the concentration of zinc is usually below 10 μg/L, and in ground waters, 10–40 μg/L (Elinder, 1986). In tap water, the zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings (Nriagu, 1980). The recommended dietary allowance for adult men is set at 15 mg/day, for adult women 12 mg/day, for formula-fed infants 5 mg/day, and for preadolescent children 10 mg/day (Cousins and Hempe, 1990). Zinc is an essential

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element in all living organisms. Nearly 200 zinc-containing enzymes have been identified, including many dehydrogenases, aldolases, peptidases, polymerases, and phosphatases (O'Dell, 1984). High zinc concentrations are found in the prostate, bone, muscle, and liver. On the other hand, zinc toxicosis has been documented in various mammalian species, mostly resulting in copper deficiency caused by excessive zinc intake (Elinder, 1986). The deficiency of Zn, which is replaced by Cd, may result in abnormal physiology disorders, and, in addition to other factors, this may have a role in mouth cancer (Kazi et al., 2010).

The subjects listed above and because of the widespread application of zinc, exact monitoring of zinc amount in the environment is needed to protect the human life. Several techniques have been employed in trace metal analysis with different degrees of success and convenience. These techniques include UV–visible spectrophotometry (Eaton et al., 1995), flame atomic absorption spectrometry (Kolachi et al., 2011) and (Afridi et al., 2011), electrothermal atomic absorption spectrometry (Percelay et al., 1988), inductively coupled plasma atomic emission spectrometry (Yamaguchi et al., 1983), total reflection X-ray fluorescence spectrometry (Mukhtar et al., 1991) and electrochemical stripping analysis (Adeloju et al., 1996). Between the different techniques, stripping analysis offers the advantages of species characterization and of utilizing inexpensive instruments and at low operating cost (Wang, 1985). Anodic stripping voltammetry (ASV) including a diversity of electrochemical approaches, has a step of pre-concentration onto the electrode surface prior to the voltammetric measurements. The major advantage of ASV compared with direct voltammetric measurement and other analytical techniques is the pre-concentration factor. Anodic stripping voltammetry (ASV) that is the most popular stripping voltammetric technique is an effective technique for the determination of trace amounts of metal ions.

2. Experimental

2.1. Reagents

Zinc nitrate, ethanol, nitric acid, hydrochloric acid, acetic acid, trifluoroacetic acid, tetraethyl orthosilicate (TEOS), ammonium hydroxide, acetone and 1-octanol were purchased from Merck (Darmstadt, Germany). Analyte, salts, solvents, acids, and bases were of analytical grade. Quinolin-8-ol (L_1) was obtained from Scharlau Chemie S.A. (Barcelona, Spain), 5,7-diiodo quinoline-8-ol (L_2) was purchased from Sigma Aldrich (St. Louis, MO, USA), 4,5-diphenyl-1H-imidazole-2(3H)-one (L_3) and 2-{[2-(2-Hydroxy-ethylamino)-ethylamino]-methyl}-phenol (L_4) were synthesized in our laboratory. The hollow fiber polypropylene membrane support Q3/2 Accurel PP (200 μm thick wall, 0.6 mm inner diameter and 0.2 μm average pore size) was purchased from Membrana GmbH (Wuppertal, Germany). The multi-walled carbon nanotubes (MWCNTs) were purchased from the Research Institute of the Petroleum Industry (Tehran, Iran). The mean diameter of the MWNTs was 10–15 nm, the length was 50–100 nm and purity >98%.

2.2. Standards and water samples

The 1000 mg/L standard stock solution was prepared by accurately weighting 3999 mg of Zinc nitrate into 1000 mL volumetric flask and dissolved in deionized water. The stock solution was diluted with deionized water to obtain 5-point calibration standard solution, 0.05, 0.5, 5, 50, and 500 ng mL^{-1}, respectively. The water samples (1.0 L) were collected from different sections of Darongar River (Dargaz, Iran). Samples were collected and stored in plastic (high density polyethylene) containers in the dark at 4 °C in refrigerator until analysis. The time between collection and analysis is less than 72 h.

2.3. Apparatus and voltammetric procedure

All of the voltammetric measurements were obtained by μAuto lab type(III) with polarography stand Model 757 VA computerace (Metrohm, Switzerland) comprising conventional three electrode arrangements such as hanging mercury drop electrode (HMDE) as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode and carbon electrode as an auxiliary/counter electrode. Voltammetric measurements of Zn (II) were performed in the DPASV-mode. The volume of the solution introduced in the voltammetric cell has been 11 mL. The solutions were de-aerated by ultrapure N_2 gas for 100 s. The voltammetric experimental variables such as deposition time, deposition potential, and scan rate of electrode potential and stirring speed of the solution were optimized. The study revealed that peak currents for analyzed metals were linearly proportional to the deposition time up to 60 s. No more increase in peak currents was observed for cations. Therefore, 60 s was selected for the determination of Zn (II). At very long deposition time, deposited metals may saturate the surface of the electrode. The effect of deposition on peak currents of Zn (II) standard solution was examined over the potential range of −0.8 to −1.15 V at a deposition time of 60 s. It was observed that the best current signal value obtained at a deposition potential of −1.15 V, and it was used for the further studies. The other DPASV optimal conditions were as follows: equilibration time 5 s, pulse amplitude 0.05005 V, pulse time 0.04 s, sweep rate 0.0149 V S^{-1}, stirring rate 2000 rpm. Operational mode differential pulse, voltage step 0.005951 V and voltage step time 0.4 s. A digital pH meter model 744 (Metrohm Instruments) with a glass electrode was used for all pH measurements. Stirring of the solutions was carried out by a Biocate STUART CB302 magnetic stirrer, Ukraine.

2.4. HF-SLPME fiber fabrication

2.4.1. Carbon nanotube functionalization

1000 mg of raw MWCNT was refluxed in 100 mL mixture of concentrated H_2SO_4/HNO_3 (3:1v/v) at 80 °C for 6 h. Then the mixture was washed by deionized water until the pH of the solution reached 7.00. Then the solution was filtered and dried at 60 °C for 4 h to obtain the carboxylated MWCNTs (COOH-MWCNTs) (Fig. 1).

2.4.2. Sol–gel process

The sol–gel solution was prepared as follows: first to initiate the hydrolysis, 640 μL of TEOS, 130 μL of TRIS aqueous solution (5%) as base catalyst and 500 μL of EtOH were added into a polypropylene micro centrifuge vial and the mixture stirred and heated at 70 °C for 2–3 h until a homogeneous solution is formed. Then 20 μL of concentrated ammonium hydroxide was added to the micro centrifuge vial. The mixture

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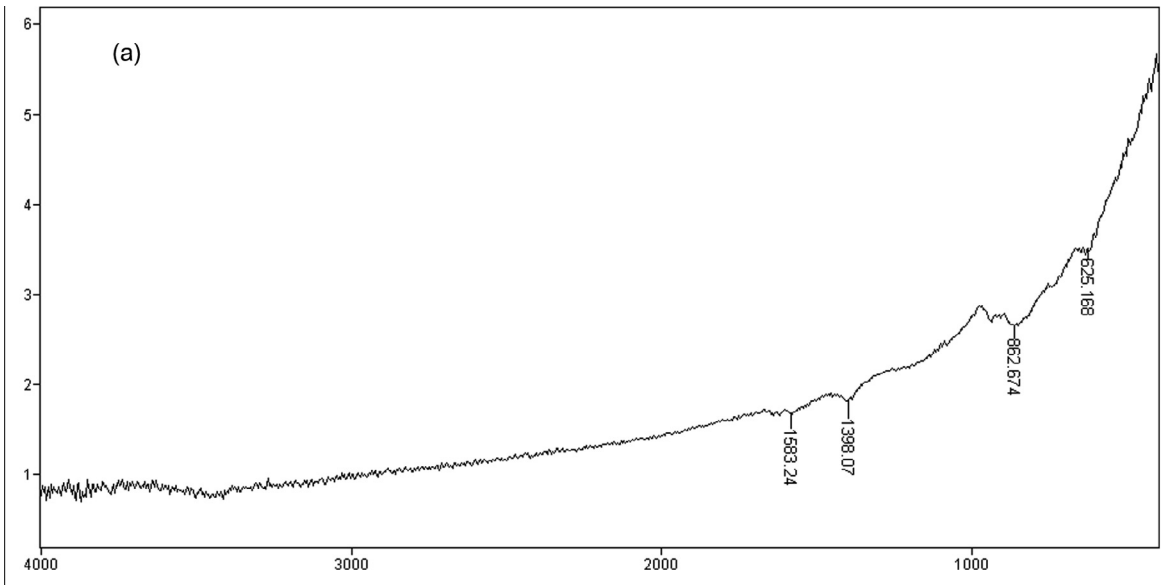

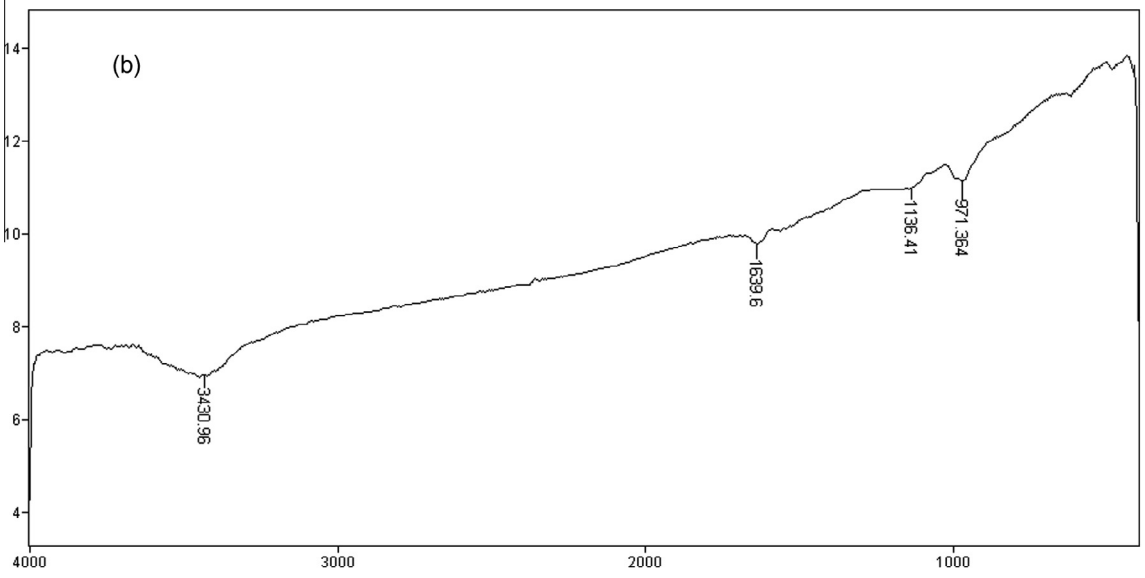

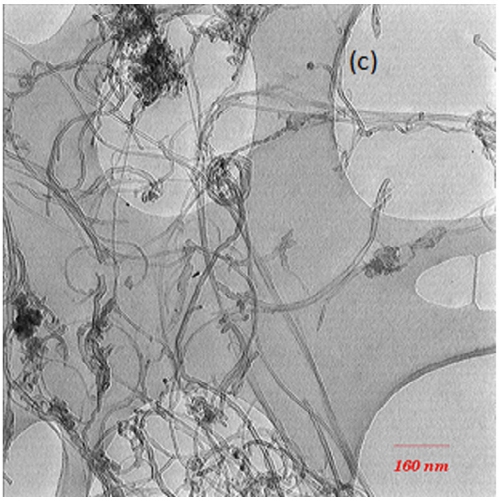

Figure 1 (a) FT-IR spectra of untreated MWCNTs, (b) FT-IR spectra of acid-functionalized MWCNTs (MWCNT-COOH), (c) transmission electron microscopy (TEM) of raw MWCNT.

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was centrifuged at 3000 rpm for 5 min. The top clear solution was removed and the synthesized gel at the bottom of the tube was washed sequentially twice with deionized water and once with ethanol to remove the un-reacted reactant and excess catalyst. The resulting gel was transferred to a clean vial and dispersed in 1 mL 1-octanol and then used for fabrication of fiber.

2.4.3. Fabrication of the sol–gel/MWCNT/SLPME device

0.04 g of functionalized MWCNTs was dispersed in 1 mL 1-octanol/ethanol (1:1 v/v) mixture. Then the synthesized gel was dispersed in this mixture. Hollow fiber was cut into segments in a length of 1.5 cm. The fiber segment was cleaned with acetone to remove impurities and directly dried in air. Then, the fiber was submerged in 1-octanol for a few seconds to fill the membrane pores of the hollow fiber wall. After that, 3.0 μL of the acceptor phase (sol–gel/MWCNTs) was injected inside the hollow fiber with a microsyringe. The fiber surface was washed with water to remove excessive organic solvent. Then the segments were sealed at both ends by 2.5 mm tip of tack as stoppers (Fig. 2).

2.5. Extraction and pre-concentration of Zn (II) procedure

This fiber was placed into the 5 mL of sample solution present in a proper vial (25 mL volume). The vial was placed on a magnetic stirrer for 60 min at the appropriate agitation speed, 200 rpm. In this procedure the analytes from the sample solution (donor phase) diffuse through the porous polypropylene membrane into the acceptor solution inside the fiber. When extraction completed at its time, the hollow fiber was taken out from the vial and transferred into a glass vial containing 3.0 mL of HNO_3(1 M):MeOH (70:30 v/v) mixture and the analytes were desorbed from fiber by stirring for 30 min at the appropriate agitation speed, 150 rpm. Then the 1 mL of this solution was diluted with supporting electrolyte up to 11 mL and transferred into the measurement cell for DPASV analysis. The fiber segments were disposable.

3. Results and discussion

3.1. Experimental optimization of extraction conditions

To achieve the best extraction performance, several parameters were optimized. These parameters included effect of pH, organic solvent, ligand as stripping agent, functionalized MWCNT concentration, donor phase volume, extraction time, stirring rate and desorption solvent.

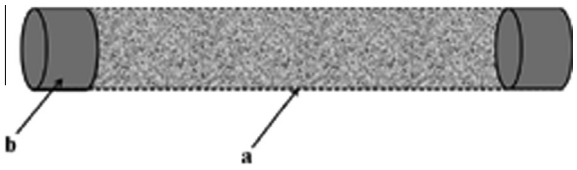

Figure 2 Simple scheme of pseudo-stir bar HF-SLPME device, (a) Filled hollow fiber membrane by sol–gel and CNT mixture (b) magnetic stoppers (iron pins; 2.5 mm × 0.6 mm);

3.1.1. Effect of pH

The pH of aqueous feed-phase plays an important role in the extraction process. The difference in acidity between the donor phase and sorbent can promote the extraction of analytes from the donor phase to the acceptor phase (Jiang et al., 2008). The final experimental results are shown in Fig. 3. As results display, when the pH value of the working solution was 5, the pre-concentration factor of Zn (II) on adsorbent is at the highest value. Extraction efficiency decreases at the higher and lower pH values. Therefore pH 5.0 was selected for further experiments. The peak current fluctuations observed in pH values less than 5.0 were attributed to the partial protonation of the ionizable species (Ganjali et al., 2007; Gupta et al., 2002). At low pH, the carboxylic groups on the sorbent were mainly in the neutral form. Thus, the interactions between the active MWCNTs and metal ions significantly decrease (Es'haghi et al., 2011). The peak current fluctuations above pH 5.0 might be justified by the formation of insoluble metal hydroxides in the solution.

3.1.2. Effect of organic solvent type used for sol dispersion

It is important to choose a suitable extracting organic solvent for an efficient extraction of target analyte from aqueous solution to pores of the hollow fiber. This organic solvent should be able to make homogeneous composite from synthesized sol as described in Section 2.3. In addition, the organic solvent should have a low solubility in water and low volatility and vapor pressure to prevent the solvent loss during the extraction and should withstand high stirring speed without leakage. Especially when faster stirring rates and long extraction time are used (Shrivas and Patel, 2011) and most important of all, those selected solvents should ensure high enrichment for tested analyte. Several dispersion solvents were investigated. According to the results, 1-octanol was found to possess higher extraction efficiency.

3.1.3. Effect of ligand as stripping agent

The objective of this study is to investigate ligand effect as stripping agent for the microextraction of Zn (II) in relation to various experimental variables. The microextraction process includes a stripping step in which metal ions adsorbed by fiber, transited to the final acceptor phase by ligand as a strippant. Stripping agent was found to be the key factor in determining

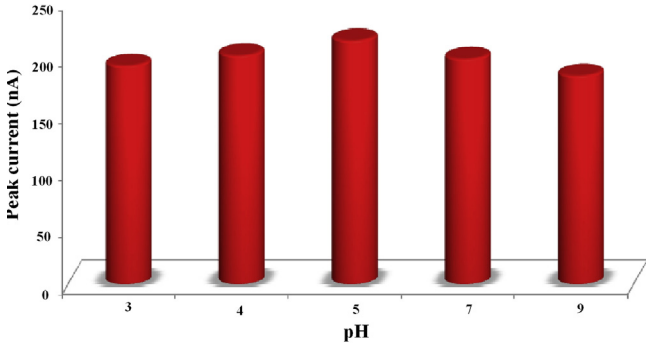

Figure 3 Effect of feed solution pH on the extraction, Conditions: analyte concentration, 50 ng mL^{-1}; donor phase volume, 5.0 mL; acceptor phase volume 3.0 μL; stirring speed, 150 rpm; extraction time, 60 min; room temperature.

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an effective system for the recovery of metal ions. In addition, application of reagents capable to complex metal ions is an alternative method for stripping the metal ions from fiber into the receiving phase. The selected agent is added to the desorption solvent, for improve analyte desorption from the fiber. This work involves complex formation between metal ions and different ligands which are used as a stripping agent. Results in Fig.4 show this agent effect. Different ligands, i.e. L_1, L_2, L_3 and L_4 were used as a stripping agent to evaluate the influence of different complexing agents to strip metal ions in the final acceptor phase. The use of ligands as stripping agent (L_1, L_2, L_3 and L_4) provides faster Zn (II) extraction and back extraction kinetics than L_0 (in the absence of ligand). It was found that L_3 for Zn (II) extractions is the most efficient stripping agent in this investigation. In relation to these three ligands, L3 has different donor groups like N and O that could be good sites for complex formation with Zn (II) ions.

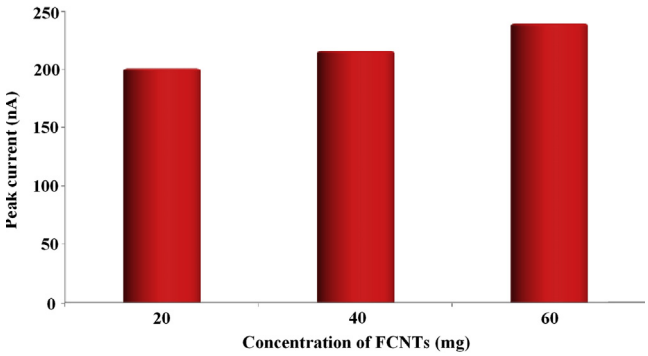

Figure 5 Effect of functionalized MWCNT concentration, Conditions: analyte concentration, 50 ng mL^{-1}; pH, 5.0; donor phase volume, 5.0 mL; acceptor phase volume 3.0 μL; extraction time, 60 min; stirring speed, 200 rpm ; room temperature.

3.1.4. Effect of functionalized MWCNT concentration

As new carbon-based nano-materials, the potential of CNTs as sorbents for the solid-phase microextraction (SPME) of environmental pollutants has been investigated in recent years. Multiwall carbon nanotubes (MWCNTs) have been successfully used as sorbent for solid phase extraction of metal ions (Hsieh et al., 2006). CNTs exhibit an extraordinary adequacy of structural, mechanical and electronic properties, which have made them potentially useful in nanotube-reinforced materials, as the sorbents for SPME and the like (Li et al., 2009). The influence of MWCNT amount on the extraction capacity has been examined to add functionalized MWCNTs at 20, 40 and 60 mg mL^{-1} in sol. As shown in Fig.5, the MWCNT concentration has a positive effect on the extraction of Zn (II) ions. The optimal concentration of MWCNTs was obtained at 60 mg mL^{-1}. At higher than 60 mg mL^{-1} MWCNT concentrations, injection of the mixture into the hollow fiber with a microsyringe was done hardly.

3.1.5. Effect of the donor phase volume

The volume of the donor phase has an important role in the solid phase extraction of the metal ions to obtain high pre-concentration factor (Ghaedi et al., 2008a,b; Parham et al., 2009; Sarafraz-Yazdi and Es'haghi, 2005). Donor phase volumes were optimized by changing the volume of the donor phase between 3 and 15 mL while the volume of the acceptor phase was kept constant at 3.0 μL. As the volume of the sample increases, the pre-concentration factor also increases (Psillakis and Kalograkis, 2003; Sarafraz-Yazdi and Es'haghi, 2006). But a larger sample volume can be disadvantageous due to poorer mass transfer kinetics that result in a poor extraction efficiency. This would lead to a decrease in the microextraction output (Psillakis and Kalogerakis, 2001; Tao et al., 2009). The results are displayed in Fig. 6. According to the results, the optimum donor phase volume was 5.00 mL.

3.1.6. Effect of extraction time

One of the most important steps in the development of the microextraction method is determination of time necessary to reach the equilibrium between the sample matrix and the coating of fiber. The effect of extraction time on the process was investigated by monitoring the peak current with exposure time over 15, 30, 45, 60 and 90 min with a sample volume of 5 mL at a room temperature. The amount of analyte that could be extracted depends on the partition coefficient of the analyte between the aqueous sample and organic solvent in the pores of the fiber wall and, subsequently, between the organic solvent and sorbent, in the lumen of the fiber, as the acceptor phase. Complete equilibrium needs not to be attained for accurate and precise analysis (Shen and Lee, 2002). The results show that the peak current commonly increased with extraction time. After 60 min, with additional extraction time, the signal became constant. Thus the time of 60 min was selected for optimum extraction time.

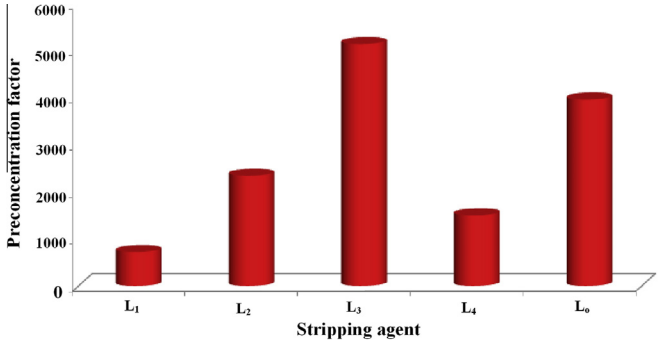

Figure 4 Effect of stripping agent: Conditions: analyte concentration, 50 ng mL^{-1}; pH, 5.0; donor phase volume, 5.0 mL; acceptor phase volume 3.0 μL; extraction time, 60 min; stirring speed, 200 rpm ; room temperature.

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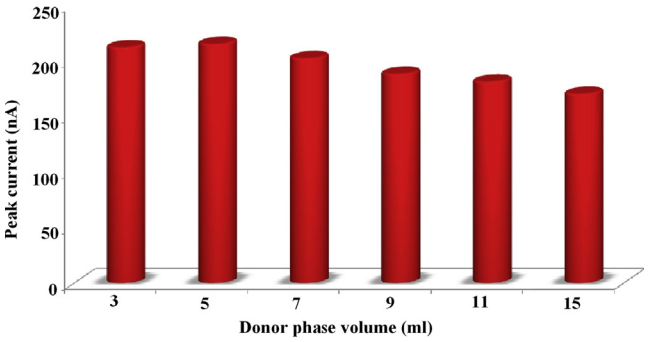

Figure 6 Effect of donor phase volume on the extraction, Conditions: analyte concentration, 50 ng mL^{-1}; pH, 5.0; acceptor phase volume 3.0 μL; stirring speed, 150 rpm; extraction time, 60 min; room temperature.

3.1.7. Effect of the stirring rate on extraction

Effect of stirring rate was studied by using a magnetic stirrer. The stirring of the hollow fiber can decrease the thickness of the diffusion film and reduce the time needed to reach equilibrium (Pedersen-Bjergaard et al., 2000). In these experiments 150, 200, 250 and 300 rpm stirring rates for extraction were investigated. The higher stirring speed than 200 led to mechanical stress of the fiber (Wen et al., 2004). The stirring speed of 200 was chosen as the optimum stirring rate for extraction.

3.1.8. Effect of desorption solvent

Desorption solvent has an important role in the amount of analyte desorption. Desorption solvent must be able to resolve the analyte and the loss of the interaction between analyte and adsorbent. Some types of solvent as the organic solvent in the extraction process were investigated including: HCl (1 N), HCl (1 N): MeOH (50:50 v/v), HNO_3 (1 N) and HNO_3 (1 N): MeOH (70:30 v/v). Consequently according to the experiment results, HNO_3 (1 N): MeOH (70:30 v/v) mixture was selected as the desorption solvent.

Table 1 Determination of Zn (II) in river water samples.

Sample	Zn (II) Conc. (ng ml^{-1})	RSD % (n = 5)
S_1	8.9	3.64
S_2	8.6	2.87
S_3	8.5	4.95
S_4	8.7	2.35
S_5	9.1	2.98
S_6	8.7	3.87
S_7	8.8	3.21
S_8	9.0	3.76
S_9	9.3	2.83
S_{10}	8.5	4.18

Table 2 Recovery tests for Zn (II) extraction with HF-SLPME coupled with DPASV under optimized conditions.

Sample	Zn (II) conc.		Recovery (%)
	Spiked (ng mL^{-1})	Found (ng mL^{-1})	
Tap water	0	36.8	–
	50	84.3	95.00
River water	0	12.5	–
	50	59.6	94.20

3.1.9. Salt effect

It has been reported that the addition of salt to the samples is beneficial for the extraction efficiency of many compounds in LLE (Marczenko, 1986) and SPME (Mohammadi et al., 2005). The experiments were conducted to evaluate the effect of ionic strength on the extraction efficiency by adding different amounts of NaCl into the samples in the range of 0–5% (w/v). Other experimental conditions were kept constant. The results showed that salt addition has no significant effect on the pre-concentration factor. Therefore, the pre-concentration factor is nearly constant by increasing the amount of

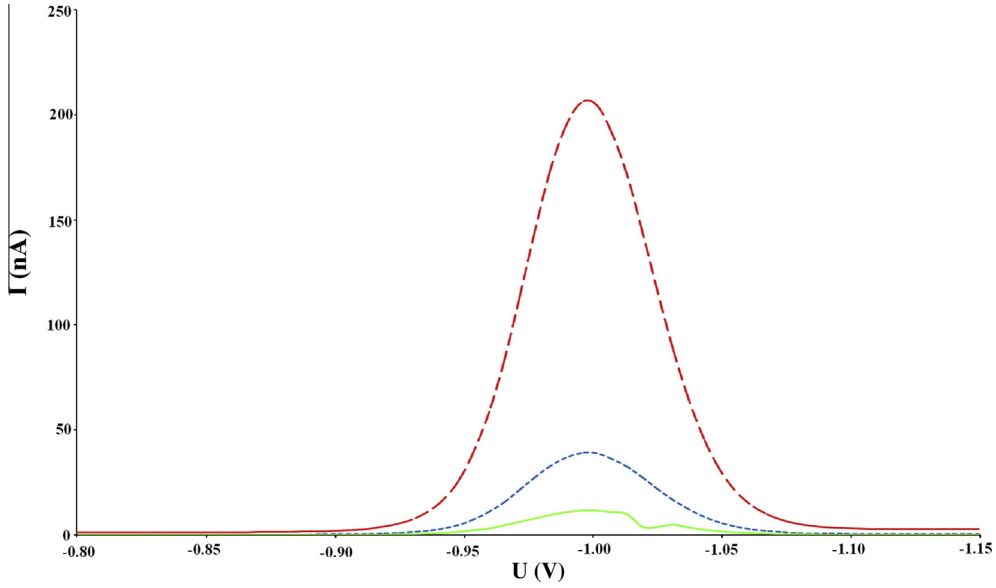

Figure 7 Differential pulse voltammogram of Zn (II) obtained from the blank voltammogram (——), River water sample (- - - -) and the same sample after microextraction under optimal conditions (——).

Table 3 Comparative data from some recent studies (researches) on pre-concentration systems for Zn (II) determinations in water samples.

Pre-concentration system	LOD[a] (μg/L)	R.S.D (%)	EF[b]	PF[c]	SV[d] (mL)	Technique	References
Multiwall carbon nanotubes	0.35	< 5.0	–	80	400	FAAS	Tuzen et al. (2008)
Modified zeolite	0.006	1.3	–	160	800	FAAS	Mostafavi et al. (2006)
Modified mesoporous silica	8.0×10^{-6} mM	< 4.0	–	200	1000	FAAS	Pérez-Quintanilla et al. (2009)
Magnetic nanoparticles modified	0.8	0.8	30	–	50	ICP-OES	Khajeh (2009)
Modified alumina coated with sodium dodecyl sulfate	0.69	1.2–1.4	–	292	–	FAAS	Ghaedi et al. (2008a,b)
Pseudo stirbar hollow fiber	0.015	3.6	–	5140	5	DPASV	This work

[a] LOD: limit of detection.
[b] Enrichment factor.
[c] Pre-concentration factor.
[d] Sample volume.

sodium chloride, and the extraction experiments were carried out without adding salt.

3.2. Quantitative evaluation and real samples

Under the optimum conditions, the linearity range, limit of detection, and repeatability of the method were investigated. The calibration equation was $y = 3.270x + 19.97$. Good correlation coefficient (R^2) with excellent linearity for target analytes was 0.998. The linearity range for the optimized procedure was between 0.05 and 500 ng mL^{-1}. Furthermore, the limit of detections (S/N = 3) was 0.015 ng $mL^{-1}$and the relative standard deviation for five replicate measurements of 50 ng mL^{-1} Zn (II) is 3.60%.

The proposed method was applied successfully to the determination of Zn (II) in the Darongar river (Dargaz, Iran). For determination of experimental pre-concentration factor, peak currents after extraction of analyte should be divided into peak currents before extraction at the same concentration and conditions. For doing this, after extraction of analyte on to the fiber containing 3 μL of sol solution, analyte was desorbed with 3.0 mL of MeOH: HNO_3 (1:1 v/v) mixture. Then the 1 mL of this solution was diluted with supporting electrolyte up to 11 mL. Thus peak current after extraction divided to peak current before extraction was multiplied by the dilution factor. The volume of the donor phase was 5.0 mL and the volume of sol solution (acceptor phase volume) was 3 μL. The proposed method was applied to Darongar (Dargaz, Iran) river water samples. As shown in Table 1 the average amounts of Zn (II) in 10 samples were found to be 8.81 ng mL^{-1}. The relative recoveries in river water and tap water samples at a spiking level of 50 ng mL^{-1} range were 94.2% and 95.0% respectively (Table 2). These results illustrated that the matrix effect was relatively low (see Fig. 7). This method was perfectly selective for heavy metals.

4. Concluding remarks

This method was applied for the determination of Zn (II) in river water samples and could be used for other aqueous samples. The polypropylene porous membrane shows high stability and adequate to be used in a method based on MWCNT reinforced sol–gel combined with ASV detection for the extraction and determination of Zn (II) with extraction and back-extraction occurring at the same time. This procedure can be successfully applied to the analysis of water samples in the study of Zn (II) contamination. A review of selected methods used in the determination of Zn(II) in water samples is shown in Table 3.

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